TITLE:	**PALLADIUM/COPPER ALLOY COMPOSITE MEMBRANES FOR HIGH TEMPERATURE HYDROGEN SEPARATION**
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OBJECTIVES

The specific objectives that we have pursued during the last year are:

- To fabricate Pd and Pd alloy composite membranes on porous stainless steel substrates, and
- To determine the permeation properties and physical and mechanical resistances of these membranes when exposed to gaseous mixtures containing such gases as CO, CO_2, H_2O and H_2S at different compositions..

ACCOMPLISHMENTS TO DATE

Recently, we have prepared Pd membranes on porous stainless steel (SS) supports from the Pall Corporation and Mott Metallurgical. For example, a ~4 μm Pd film was deposited on a ZrO_2 coated, Pall AccuSep filter (Pall-76) and the pure H_2 flux data are shown in Fig. 1. The primary challenges in preparing Pd alloy composite membranes on stainless steel supports are twofold. First, the mean pore size of the porous metal material is typically about 2 μm, requiring thicker Pd alloy films to bridge these larger pores. Second, a diffusion barrier layer is usually required to prevent intermetallic diffusion between the Pd alloy film and the stainless steel support. A strategy to mitigate both of these issues is to deposit an oxide coating on the stainless steel filter. This creates a diffusion barrier and reduces the surface roughness of the substrate. However, the oxide coating does reduce the flow through the support, and optimization of the oxide coating thickness is necessary to minimize the pressure drop through the stainless steel support. High temperature sealing is much easier with metal supports as the ends can be easily densified and sealed to a tubing system by welding, brazing, or metal compression fittings.

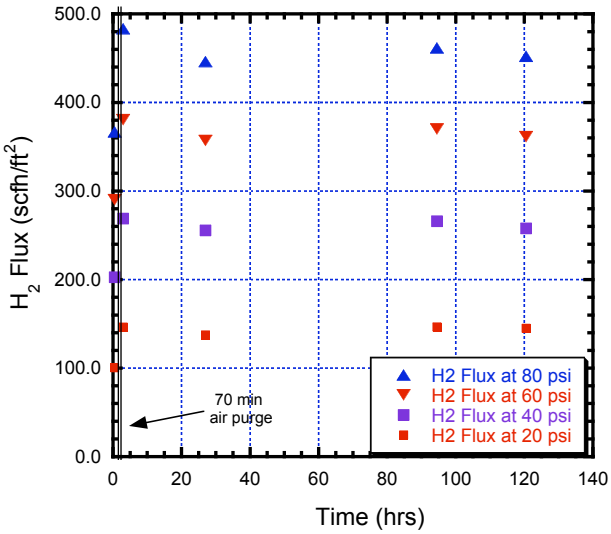

Fig. 1. The pure H_2 flux through a Pd ZrO_2/stainless steel membrane (Pall-76) at 400 °C over 5 days.

The pure H_2 flux for the Pall-76 membrane at 400 °C for a 80 psig feed gas was 440 SCFH/ft^2, **more than twice** the DOE Fossil Energy 2010 target, specified at a 100 psi differential pressure. The H_2/N_2 selectivity for Pall-76 was 800 for a 20 psig feed pressure using graphite ferrules, which we have observed to contribute to leak flow, particularly at test pressures above 40 psig. The H_2 flux is quite stable over a five day period at 400 °C, which supports our claim that the ZrO_2 layer is performing well as a diffusion barrier. Copper or gold alloy membranes can easily be prepared from these pure Pd membranes.

Given the data reported by McKinley (U. S. Patent 3,439,474) that PdAu alloys were superior to PdCu in terms of resistance to poisoning by H_2S, several PdAu alloy membranes on porous ceramic supports were made by electroless plating methods. An example is membrane GTC-31 which has an alloy composition of approximately 15 mass % Au in Pd. Permeation data over a range of pressures at 400 °C for this membrane were measured, and the pure H_2 flux at 100 psig feed pressure was 245 SCFH/ft^2, also **exceeding** the DOE Fossil Energy 2010 target. The ideal $H_{2/}N_2$ selectivity for this membrane was 279 at 100 psig feed pressure. When mixture experiments with the water gas shift (WGS) feed were performed with the PdAu membranes, essentially no inhibition of the hydrogen flux was observed. H_2S tests with PdAu membranes will be performed prior to the end of our current grant period.

FUTURE WORK

- Continue working with Pall AccuSep ZrO_2 coated stainless steel substrates in order to duplicate the performance of Pd alloy membranes supported on porous ceramic filters,

LIST OF PAPERS PUBLISHED, PRESENTATIONS, STUDENTS SUPPORTED

JOURNAL ARTICLES AND CONFERENCE PROCEEDINGS

Kulprathipanja, A., Alptekin, G. O., Falconer, J. L. and J. D. Way, "Pd and Pd-Cu Membranes: Inhibition of H_2 Permeation by H_2S," *Journal of Membrane Science*, **254**, 49-62(2005).

Thoen, P. M., Roa, F., and J. D. Way, "High Flux Palladium-Copper Composite Membranes for Hydrogen Separations," *Desalination*, accepted.

Roa, F. Thoen, P. M., Way, J, D., DeVoss, S., and G. Alptekin, "Effect of CO_2, CO, H_2S and Sweep Gas on the Hydrogen Flux of a Pd-Cu Alloy Membrane," *ACS Symposium Series, Membranes for Fuels and Energy*, accepted, 7/05.

Gade, S. K., Keeling, M. K., Steele, D. K., Way, J. D., and P. M. Thoen, "High Flux Pd and Pd Alloy Membranes Deposited on Stainless Steel Supports by Electroless Plating," Proceedings of ICIM 9, Lillehammer, Norway, June 2006.

Gade, S. K., Thoen, P. M., Keeling, M. K., Steele, D. K., and J. D. Way, "Sulfur Resistant Pd-Au Composite Membranes for H_2 Separations," Proceedings of ICIM 9, Lillehammer, Norway, June 2006.

CONFERENCE PRESENTATIONS

High Flux Palladium-Copper Composite Membranes for Hydrogen Separations, Talk given by Paul Thoen, International Conference on Membranes (ICOM), Seoul, Korea, 8/05.

High Flux Palladium-Copper Composite Membranes for Hydrogen Separations, China/USA/Japan Chemical Engineering Conference, Beijing, China, 10/05. (Invited presentation)

STUDENTS SUPPORTED

Sabina K. Gade, Ph. D. candidate